NASA TM- 86431

NASA Technical Memorandum 86431

AN INVESTIGATION OF MOLECULAR STRUCTURE OF COPOLYMERS USING POSITRON ANNIHILATION SPECTROSCOPY

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MAY 1985

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SUMMARY

We have studied molecular characteristics of two linear aromatic polyimides, and a copolyimide containing equal mole fractions of the two, using Positron Annihilation Spectroscopy. It is found that the copolyimide is characterized by mass and electron densities higher than the average of the values for its constituents and permits both bound and unbound entry of water into it. These results, coupled with the observations that the copolyimide also exhibits thermo-mechanical and physical properties that differ from the average of the values for its constituents, imply that the copolyimide contains regions of transition where the molecular architecture is rather different from that of its constituent polymers.

INTRODUCTION

When two homopolymers are combined, they form a new type of macromolecule - a copolymer. These copolymers have material properties that may be quite different from those of the constituent homopolymers[1]. It is thus possible to develop copolymers with properties otherwise unattainable with individual polymers. In order to develop a proper understanding of copolymers with desirable characteristics, it is imperative that all possible structural/architectural information be obtained about the individual components as well as the resultant complexes.

Burks et al.[2] recently developed copolyimides from selected linear aromatic polyimides. They found that copolyimides made from BDSDA/ODA and BDSDA/MPD homopolymers exhibited moderate flows like BDSDA/MPD, had tensile properties similar to those of BDSDA/MPD but had glass transition temperatures (T_g) lower than the average value of their constituents and showed a slow change in specific heat (C_p) with temperature in marked contrast to its constituents.

In order to elucidate the mechanisms responsible for these rather unusual properties of the BDSDA/ODA/MPD copolyimides, positron annihilation characteristics and related properties have been measured in the copolyimides as well as the constituent homopolymers. These results and their implications are discussed in the following sections.

LIST OF SYMBOLS

BDSDA	4,4' - bis(3,4 - dicarboxyphenoxy) diphenylsulfide dianhydride
ODA	4,4' - diaminodiphenyl ether
MPD	1,3 - diaminobenzene (m-phenylene diamine)
BDSDA/ODA	Homopolymer containing equal mole fractions of BDSDA and ODA
BDSDA/MPD	Homopolymer containing equal mole fractions of BDSDA and MPD
BDSDA/ODA/MPD	Copolyimide containing equal mole fractions of BDSDA/ODA and BDSDA/MPD homopolymers

DMAC	N,N - Dimethyl acetamide
n-Heptane	$[CH_3(CH_2)_5CH_3]$
w/o	Weight percent
τ_1	Lifetime of short lifetime component in the positron annihilation spectrum
τ_2	Lifetime of long lifetime component in the positron annihilation spectrum
I_2	Intensity of the long lifetime component in the positron annihilation spectrum
Na^{22}	Sodium-22 (Positron emitting isotope of sodium)
μc	Microcurie - a unit of radioactivity equalling 3.7×10^4 disintegration/sec
T_g	Glass transition temperature
C_p	Specific heat at constant pressure
Ps	Positronium
PAS	Positron Annihilation Spectroscopy

EXPERIMENTAL PROCEDURE AND RESULTS

BDSDA/ODA and BDSDA/MPD homopolymers and copolyimides containing different mole fractions of these components were prepared by allowing appropriate amounts of BDSDA, 4,4'-ODA and MPD to react in DMAC at room temperature in the manner detailed in reference 2. Moldings in the form of 2" diameter x 0.1" discs were made for each specimen.

Figure 1 shows a molecular chain arrangement for the two homopolymers and copolyimides made from them.

(a) Measurement of Saturation Moisture Content. The specimens were saturated with water by immersing them in distilled water at 90°C for several days till their weights became constant. The specimens were then desiccated in a vacuum oven at 100°C for several days till there was no further decrease in their weights. The saturation moisture contents of the specimens were then determined by comparing the corresponding saturated and desiccated weights. The results are summarized in Table I.

TABLE 1

Summary of Saturation Moisture Contents of the Specimens

No.	Specimens	Saturation Moisture Content
1	BDSDA/ODA	1.385±0.003 w/o
2	BDSDA/ODA/MPD (50-50)	1.474±0.003 w/o
3	BDSDA/MPD	1.490±0.003 w/o

(b) Measurement of Density. The densities of various desiccated specimens were determined by measuring their weights in air using a highly sensitive balance and their volumes using the buoyancy technique in an n-Heptane $[CH_3(CH_2)_5CH_3]$ medium. The buoyancy measurements were made at room temperature and required approximately 15 minutes per sample. It is thus highly unlikely that the specimen weights were affected by Heptane diffusion into them. The results are summarized in Table II.

TABLE II

Summary of Specimen Densities

No.	Specimens	Density
1	BDSDA/ODA	1.3462±0.0010 gm/cc
2	BDSDA/ODA/MPD (50-50)	1.3623±0.0003 gm/cc
3	BDSDA/MPD	1.3730±0.0005 gm/cc

(c) Measurement of Positron Annihilation Characteristics. Positron annihilation has frequently been interpreted[3,4] in the framework of Brandt's free volume model[5]. Since the relative concentrations of the constituents in the copolymers may be expected to determine the size of their free volumes, it is hoped that the positron annihilation spectroscopy (PAS) might provide some useful information about the mechanisms responsible for changes in their physical properties. It might enable us to answer such questions as: (1) Are the test copolymers merely the sum of constituent polymeric chains or do they have a somewhat modified structure? (2) Does an increase in the concentration of one constituent of the copolymer result in increase in its internal surface area and consequently an increase in the free volume fraction in the transition range copolymer?

Positron lifetime measurements were made using a standard fast-slow coincidence system[6]. The time resolution of the system - as measured with a Co^{60} gamma ray source - was approximately 450 picoseconds. The test samples were fabricated in the form of 1" dia. x 0.1" thick discs. A 10 μc Na^{22} source was sandwiched between the

two sample discs and the entire source-sample assembly was placed between two scintillation counters. A typical lifetime spectrum required about 24 hours to obtain the statistics necessary for accurate deconvolution. The positron lifetime results are summarized in Table III. In the present study, rather than trying to decide how many lifetime components were present in each spectrum, we fitted all the spectra with only two components since such analyses are expected[7] to reflect the main changes in the annihilation spectra with the changing test specimen molecular structure.

TABLE III

Summary of Positron Lifetime Characteristics

No.	Specimen	τ_1(ps)	τ_2(ps)	I_2(%)
1	BDSDA/ODA	392±5	1748±75	9.1±0.5
2	BDSDA/ODA/MPD (50-50)	388±5	1680±75	6.0±0.5
3	BDSDA/MPD	385±5	1715±100	4.1±0.5

DISCUSSION

We have examined some characteristics of the copolymers synthesized from BDSDA/ODA and BDSDA/MPD homopolymers. It has been found that the saturation moisture content as well as the density of the BDSDA/ODA/MPD (50-50) copolymer are higher than the average of the values for its constituents. These data imply the existence of a transition region in the copolyimide, characterizied by a more compact molecular architecture which permits both free and bound water entry. Such a transition regiom may be expected to have a higher molecular electron density which will not only reduce the probability of positronium formation but also increase the probability of positronium decay after its formation. An examination of the data shown in Table III indicates that this is exactly the case. The probability of positronium formation, indicated by the intensity of the long lifetime component, in the copolyimide is less than the average of the values in its constituents. The probability of positronium decay, indicated by the long lifetime component lifetime, in the copolyimide is also higher than the average of the values for its constituents.

Another noteworthy result is the observation[2] that the copolyimide glass transition temperature (T_g) ranged from (224±1)°C to (217±1)°C as the BDSDA/ODA fraction was changed from 0 to 100%. It was the lowest [(216±1)°C] for the BDSDA/ODA/MPD (50-50) copolyimide, in disagreement with an empirical equation of Wood which has been reported to have wide applicability to random copolymers[8]. This feature also indicates that the copolyimide structure is characterized by a molecular transition region different from those of its constituents.

CONCLUDING REMARKS

We have investigated the microstructural and electronic characteristics of BDSDA/ODA/MPD copolymers. It is found that the copolyimide containing equal mole fractions of its two constituent homopolymers is characterized by a transition region which is more tightly bound, has a higher molecular electron density, and permits bound as well as free water entry into it. The presence of this transition region imparts rather unique properties to the copolyimide.

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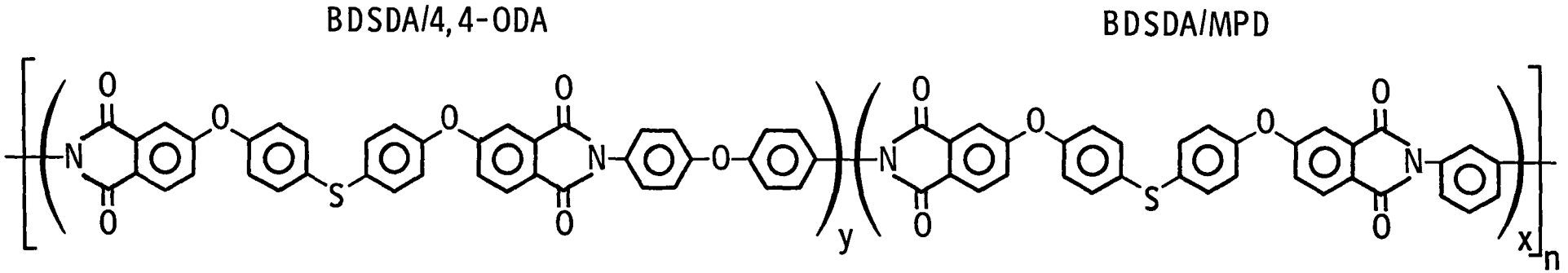

For 413 copolyimide, y = 1, x = 3

For 422 copolyimide, y = 2, x = 2 (50-50 copolymer)

For 431 copolyimide, y = 3, x = 1

Figure 1. - Molecular structure of the BDSDA/ODA/MPD copolyimide.

1 Report No	2 Government Accession No	3. Recipient's Catalog No
NASA TM-86431		

4 Title and Subtitle	5 Report Date
An Investigation of Molecular Structure of Copolymers Using Positron Annihilation Spectroscopy	May 1985
	6. Performing Organization Code 505-33-90-01
7 Author(s) Jag J. Singh, Terry L. St. Clair, William H. Holt, and W. Mock, Jr.	8 Performing Organization Report No
	10 Work Unit No
9 Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665	11 Contract or Grant No
	13 Type of Report and Period Covered Technical Memorandum
12 Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546	14 Sponsoring Agency Code

15 Supplementary Notes

16 Abstract

Positron lifetime measurements have been made in copolyimides synthesized from linear BDSDA/ODA and BDSDA/MPD homopolymers. The probability of positronium formation as well as its subsequent lifetime are lower in the BDSDA/ODA/MPD (50-50) copolyimide,indicating the presence of a transition molecular architecture characterized by higher electron density and stronger bonds which permit both chemical as well as physical entry of water molecules into it. The presence of this transition region imparts unique physical and mechanical properties to the copolyimide.

17 Key Words (Suggested by Author(s))	18 Distribution Statement
Copolyimides, Transition Molecular Structure, Glass Transition Temperature, Free Volume, Positron Lifetime, Positronium Formation Probability Electron Density	UNCLASSIFIED - UNLIMITED Subject Category - 24

19 Security Classif (of this report)	20 Security Classif (of this page)	21. No of Pages	22 Price
UNCLASSIFIED	UNCLASSIFIED	7	A02

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